INVESTIGATION OF THE PROTON DONOR CAPACITY OF ALIPHATIC N-NITROAMINES BY THE METHOD OF IR SPECTROSCOPY. THERMODYNAMIC PARAMETERS OF COMPLEXES WITH A HYDROGEN BOND.

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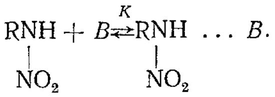
Earlier it was shown [1] that the complexes formed in the interaction of one of the representatives of the series of alkyl-N-nitroamines (NA) – methylnitroamine – with aliphatic secondary and tertiary amines may have both molecular and ionic structures. In relatively nonpolar solvents, complexes with an ionic structure exist in the form of ion pairs, formed when a proton is transferred from a NA molecule to a base. For a quantitative study of this process, information is needed on the ability of N-nitroamines to participate as proton donors in the formation of a hydrogen bond, the important role of which in processes of protein transfer has been noted in a number of investigations (see, for example, [2]). This information is especially important in the case of NA, since for them proton transfer occurs at an appreciably lower strength of the H-bond in comparison with OH acids. Therefore, at the first stages of a study of the process of proton transfer in the series of aliphatic N-nitroamines under conditions of weak solvation, it was advisable to investigate the process of formation of a hydrogen bond with proton acceptors that form H-complexes only of a molecular structure with N-nitroamines:



$$\underset{\mathrm{NO_2}}{\underset{|}{\mathrm{RNH}}} + B \overset{K}{\rightleftarrows} \underset{\mathrm{NO_2}}{\underset{|}{\mathrm{RNH}}} \ldots B. \qquad (1)$$

In this work the thermodynamic parameters of H-complexes of a series of substituted alkyl-N-nitroamines with a series of proton acceptors: benzaldehyde (BA), acetonitrile-D_3 (AN-D_3), cyclohexanone (CH), p-dimethylaminobenzaldehyde (DMAB), dimethylformamide (DMFA), dimethylacetamide (DMAA), dimethyl-D_6 sulfoxide (DMSO-D_6), and hexamethylphosphoramide (HMPA) were measured in a solution with CCl_4, and they were compared with the parameters of H-complexes of other NH and OH acids. The measurements were performed on a PE-457 two-beam spectrophotometer, equipped with a supplementary electronic attachment [3] for recording spectral information in digital code on perforated tape, which speeds up the treatment of the data obtained on a computer. Quartz calibrated cuvettes with CaF_2 windows were used for the measurement; the cuvette thickness was varied from 0.01 to 5.0 cm. In the recording of the spectra, solutions of acceptors in CCl_4 of the same concentrations as in the investigated solution were placed in the reference channel. Both cuvettes were in a hermetic thermostatically controlled cell; during the experiment constancy of the temperature was maintained with an accuracy of $\pm 0.2°C$, monitoring with a digital voltmeter and a thermocouple placed on the wall of the cuvette. The investigated substances were dried thoroughly; the preparation of the solutions and filling of the cuvettes were performed in a dry box, dried with phosphorus pentoxide and purged with dry nitrogen. Redistilled cp grade CCl_4 and dried zeolite 4A were used for the work. The absence of water in the solvent was monitored according to the IR absorption spectra in the region of 3500-3800 cm^{-1} at a cuvette thickness of 5 cm. Dimethyl-D_6 sulfoxide was redistilled twice under vacuum; acetonitrile-D_3 after prolonged boiling over P_2O_5, was redistilled over a fresh portion of phosphorus pentoxide and then over potash. p-Dimethylaminobenzaldehyde was recrystallized twice from chloroform and dried in air. The remaining bases were purified by the well-known methods [4]. All the liquid bases were stored over zeolite. Solid alkyl-N-nitroamides were recrystallized twice from suitable solvents and dried under vacuum; the liquid compounds were redistilled under vacuum over P_2O_5. The degree of purification of the substances was monitored chromatographically.

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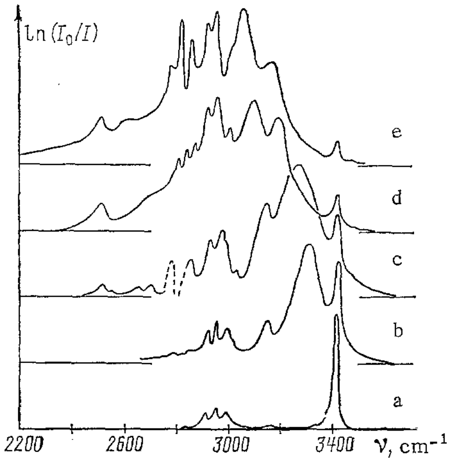

Fig. 1. Absorption spectra of solutions of methylnitroamine and proton acceptors in CCl_4. Without acceptor (a), with AN-D_3 (b), with DMAB (c), with DMSO-D_6 (d), and with HMPA (e).

TABLE 1. Spectral Parameters of the Band νNH of Monomers of Primary Aliphatic N-Nitroamines $RNHNO_2$

Compound No.	*R*	A, liters/mole·cm²	ν_{max}, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}
I	$(CH_3)_3C$	6900	3393	25
II	Cyclo-C_6H_{11}	6400	3397	32
III	C_4H_9	9000	3407	34
IV	C_3H_7	9300	3405	32
V	CH_3	9700	3416	21
V*I*	$N{\equiv}CCH_2CH_2$	11100	3406	29
V*II*	$(NO_2)_3CCH_2CH_2$	12200	3403	25
V*III*	C_2H_5OCO	15200	3407	32
IX	*p*-CH_3O—C_6H_4—SO_2	19400	3384	50

The NA concentration was selected considering solubility in CCl_4 and was varied in the range $0.2 \cdot 10^{-3}$–0.25 M; the concentration of the proton acceptors was varied from $0.5 \cdot 10^{-2}$ to 1.0 M. Discrete recording of the spectrum was performed at various intervals of wave numbers, the value of which varied depending on the widths of the investigated bands, in accordance with the recommendations of [5]. The spectral slit widths did not exceed 1 cm^{-1}, which ensured recording of the bands without apparatus distortions. The integral intensity of the bands of νNH was calculated according to the Simpson formula on a small Mir-2 computer; the region of integration for single bands was approximately 10 times the width of the band.

In the absence of proton acceptors, with sufficient dilution of the solution in the region of 3000-3500 cm^{-1}, only one narrow band of the stretching vibration of the NH group, corresponding to free nitroamine molecules, is visible in the IR spectrum of the nitroamines* (Fig. 1a). The value of the absorption coefficient at the maximum decreases with increasing temperature, whereas the integral absorption coefficient and the position of the maximum do not depend on the temperature within the range of experimental accuracy. These values, as well as the widths of the bands $\Delta\nu_{1/2}$ of the investigated nitroamines, are cited in Table 1.

With increasing NA concentration, appreciable absorption appears in the region of 3100-3300 cm^{-1}, related to the autoassociated form of NA; therefore the concentrations of the reagents were selected such that the degree of autoassociation did not exceed 1%. When a proton acceptor is added to the solution, changes in the spectral picture typical of H-complexes occur in the region of 2000-3600 cm^{-1}: a substantial increase in the integral intensity and width of the band of the stretching vibration νNH and a shift of it in the low-frequency direction (Fig. 1). The absence of bands characteristic of NA anions in the region of 1000-2000 cm^{-1} is evidence that with all the investigated bases the complexes have only a molecular structure. When the concentrations of the acid and base are varied within wide limits (by three orders of magnitude), the form of the

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*There is still another weak band in the region of 3160 cm^{-1}, belonging to the overtone of the antisymmetrical vibration of the NO_2 group.

TABLE 2. Constants of Formation of H-Complexes of Primary Aliphatic N-Nitroamines with Bases in CCl_4 at 20°C (in liters/mole)

Compound No.	BA	AN-D_3	CH	DMAB	DMFA	DMAA	DMSO-D_6	HMPA	σ^*
I	—	—	—	—	—	—	150	—	—0,30
II	—	—	8,1	15	57	72	180	500	—0,25
III	3,9	5,3	11	13	67	120	280	850	—0,13
IV	3,9	5,3	13	16	60	120	280	870	—0,11
V	3,8	7,3	15	20	87	120	350	1600	0
V*I*	15	24	64	74	480	1000	2300	11000	0,50
V*II*	18	27	82	140	980	1300	3500	25000	0,61
V*III*	—	5,7	17	32	150	200	500	3500	2,00
*I*X	—	—	—	—	—	—	1900	—	~4

contour of the band νNH of the complex remains unchanged, which indicates that under the investigated conditions only one type of complexes with stoichiometric composition 1 : 1 exists in the system.

The constants of formation of the bimolecular complex K were calculated by a method convenient for direct treatment of spectral information on a computer. The integral optical density D, measured in any arbitrarily selected spectral interval $\Delta\nu$ under the experimental conditions enumerated above, can be written in the form

$$D = d(A_A C_A + A_K C_K + A_B(C_B - C_B^0)), \tag{2}$$

where d is the cuvette thickness; A_A, A_B, and A_K are the integral absorption coefficients of proton donors and acceptors and H-complexes, respectively, within the selected spectral interval; C_K is the concentration of H-complexes; C_A and C_B are the concentrations of free molecules of the corresponding reagents (C^0 is the initial reagent concentration).

Considering the condition

$$C_B^0 = C_B + C_K, \tag{3}$$

we obtain

$$D = d(A_A C_A + (A_K - A_B) C_K) = d(A_A C_A + A_K' C_K), \tag{4}$$

where A_K' is a constant for a given complex.

To determine the equilibrium constant K it is sufficient to perform two measurements of D at various reagent concentrations. In this case we obtain a system sufficient for finding the value of K and the unknown quantity A_K':

$$\left.\begin{aligned} D_i &= d_i(A_A C_{iA} + A_K' C_{iK}) && (5a)\\ C_{iA}^0 &= C_{iA} + C_{iK} && (5b)\\ C_{iB}^0 &= C_{iB} + C_{iK} && (5c)\\ C_{iK} &= K C_{iA} C_{iB} && (5d) \end{aligned}\right\} \quad i = 1,\ 2.$$

The value of the interval $\Delta\nu$ in expression (5a) is determined by the experimental conditions and is limited by the transparency of the solvent–dissolved substances system. It is desirable to select this interval large enough to reduce the influence of such a spectrophotometer error as the nonreproducibility in the wave number scale. Moreover, linear independence of Eqs. (5a) and (5b) requires observance of the inequality $A_A \neq A_K'$, which is equivalent to the condition

$$|D - d_i A_A C_{iA}^0| \gg 0 \quad i = 1,\ 2, \tag{6}$$

which can always be fulfilled by suitable selection of the interval of integration. In this case the interval $\Delta\nu$ was selected just as in the determination of the integral absorption coefficients, which permitted the use of the quantity cited in Table 1 as A_A. The system of equations (5) was solved by an iteration method with initial approximation $C_{1A} = 0$.

In contrast to the known methods of calculating K, which are applicable only at definite ratios of the concentrations of particles participating in the equilibrium (see, for example, [6]), the proposed method of calculation can be used practically any reagent concentrations and does not require separation of the overlapping bands of the vibrations of the free molecules and complexes.

TABLE 3. Thermodynamic Parameters of H-Complexes of Primary Aliphatic N-Nitroamines with Bases in CCl_4 (ΔH^0 in kJ/mole, ΔS^0 in J/(mole · deg))

Compound No.	BA		AN-D_3		CH		DMAB		DMFA		DMAA		DMSO-D_6		HMPA		pK_a [11]
	ΔH°	ΔS°	ΔH°	ΔS°	ΔH°	ΔS°	ΔH°	ΔS°	ΔH°	ΔS°	ΔH°	ΔS°	ΔH°	ΔS°	ΔH°	ΔS°	
I	—	—	—	—	—	—	—	—	—	—	—	—	24	41	—	—	6,59
II	—	—	—	—	13	28	15	29	21	39	22	40	25	44	24	31	6,63
III	12	28	11	24	14	29	17	36	22	41	23	40	26	41	26	32	6,43
IV	11	27	12	26	15	31	16	31	21	38	25	44	25	39	24	26	6,35
V	11	27	11	21	15	29	17	33	24	44	26	46	26	42	28	34	6,23
VI	13	23	13	18	20	34	22	39	25	35	27	34	29	36	32	31	5,27
VII	14	23	16	27	20	32	24	40	30	44	31	46	31	38	34	26	4,97
VIII	—	—	17	44	19	42	24	52	27	49	27	49	28	43	33	45	3,36
IX	—	—	—	—	—	—	—	—	—	—	—	—	32	45	—	—	—

The calculated values of the equilibrium constants proved independent of the initial reagent concentrations, within the limits of the experimental error, for all the investigated systems except for cyclohexanone. In this case the values of K had a distinct tendency to increase with increasing reagent concentrations, which indicates the existence of more complex associates in the system. Therefore, the equilibrium constants for the NA—cyclohexanone systems were measured in highly dilute solutions, when the concentrations of the more complicated complexes can be neglected.

Thus, it can be asserted that the quantitative parameters of the investigated equilibria that we measured (Table 2) characterize the formation of H-complexes of NA with proton acceptors with a 1 : 1 stoichiometric composition. From the temperature dependence of the constants of complex formation, measured at the temperatures 10, 20, 30, 40, and 50°C, we calculated the values of the enthalpy and entropy of formation of H-complexes (Table 3). Each value was obtained as an average of several (4-7) independent measurements, performed at different times and with different lots of reagents. The errors of the values cited in the tables, calculated for the α = 0.9 probability level, do not exceed 2 kJ/mole for the enthalpy, 4 J/(mole · deg) for the entropy, and 10% for the equilibrium constants.

From Tables 2 and 3 it can be seen that both the ability to form H-bonds and the strength of the H-complexes in a series of alkyl-N-nitroamines have a tendency to increase with increasing basicity of the proton acceptors and increasing acidity of NA. However, in the later case this increase is not monotonic; for certain NA the correlation between the acidity and the proton donor capacity in the H-bond is violated (see, for example, compounds VII and VIII).

For a quantitative characterization of the patterns noted, we investigated the correlations between the logarithms of the constants of formation of H-complexes of various NA with the same bases (Fig. 2). As can be seen from the graphs, for all the investigated NA a distinct linear correlation is fulfilled; the parameters of the correlation equations

$$\lg K^{t^\circ}_{RNHNO_2} = m \cdot \lg K^{t^\circ}_{CH_3NHNO_2} + c \qquad (7)$$

do not depend on the temperature within the investigated region; their values are cited in Table 4. The slopes m in this case characterize the relative proton donor capacity in the series of NA (relative to methylnitroamine), and, with the exception of nitrourethane, they vary in direct correlation with the acidity. The nitroamines can be compared analogously in proton donor capacity with other NH and OH acids. Figure 3 presents the correlation between log K for H-complexes of methylnitroamine and p-fluorophenol with the same bases. A distinct linear correlation is also fulfilled here; its equation takes the form

$$\lg K^{20^\circ}_{CH_3NHNO_2} = (0{,}97 \pm 0{,}05)\, pK_{HB} - (0{,}15 \pm 0{,}11), \quad r = 0{,}992, \; s = 0{,}12, \; n = 8. \qquad (8)$$

A comparison of the slope obtained with the known values of m for all the investigated acids, lying in the range 0.5-1.2 [7], shows that the NA are medium-strength proton donors (methylnitroamine is approximately equal to phenol, for which m = 0.97, in proton donor capacity), which confirms the conclusion that we drew on the basis of the shift of the band νNH of the complex [1].

For a quantitative determination of the influence of the inductive effect on the proton donor capacity of primary N-nitroamines, the values of log K were correlated with the Taft σ^* constants of the substituents (Fig. 4a, Table 5). As can be seen from the data cited, a good linear correlation is fulfilled for compounds I-VII. The values of the slope ρ, characterizing the sensitivity of substituents in a given reaction series to the

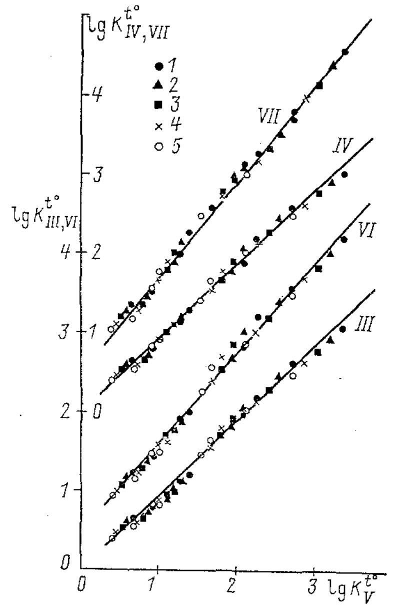

Fig. 2

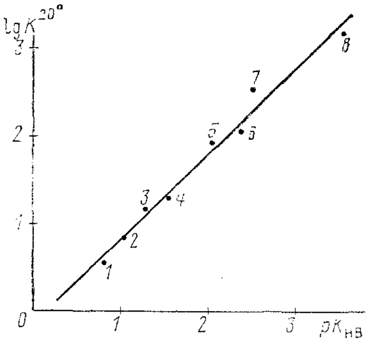

Fig. 3

Fig. 2. Dependence of the values of log $K^{t°}$ for H-complexes of a series of N-nitroamines on log $K^{t°}$ for H-complexes of methyl nitroamine with the same bases in CCl_4. III, IV, VI, and VII correspond to the numbers of the compounds in Table 1. T = 10 (1), 20 (2), 30 (3), 40 (4) and 50°C (5).

Fig. 3. Dependence of the values of log $K^{20°C}$ for H-complexes of methyl nitroamine on pK_{HB} (pK_{HB} = log K for H-complexes of p-nitrophenol with proton acceptors in CCl_4 [7]). 1-8 correspond to the numeration of the proton acceptors in Table 2.

TABLE 4. Parameters of the Correlation Equations $\log \cdot K^{t°}_{RNHNO_2} = m \cdot \log K^{t°}_{CH_3NHNO_2} + c$

Compound No.	*m*	*c*	*r*	*s*
II	0,87±0,02	0,002±0,04	0,994	0,07
III	0,96±0,015	—0,05 ±0,03	0,997	0,07
IV	0,95±0,01	—0,01 ±0,02	0,997	0,06
V*I*	1,15±0,015	0,45 ±0,03	0,996	0,08
V*II*	1,23±0,015	0,49 ±0,03	0,997	0,08
V*III*	1,15±0,02	—0,13 ±0,04	0,995	0,09

polar effect, vary with the proton acceptor capacity of the base. The coefficients m, characterizing the change in the proton donor capacity in the series of NA, and the enthalpies of formation of H-complexes are also satisfactorily correlated with the σ^* coefficients (Fig. 4b, c). Thus, NA obey the general law established for other donors in the formation of a H-bond: changes in the proton donor capacity and the value of the H-bond energy are due to the inductive influence of substituents and vary according to the quantitative characteristics of this effect [8].

Compounds VIII and IX, the substituents of which can enter into conjugation with the reaction site, deviate from the correlations discussed. Substantial deviations from linearity are observed for them, in the direction of a decrease in the proton donor capacity (for N-complexes of compounds VIII and IX with DMSO-D_6, the free energy is lowered by 16 and 30 kJ/mole, respectively). This effect clearly contradicts the data obtained for other proton donors. Thus, in the case of H-complexes of substituted phenols with dimethylacetamide, a linear dependence of log K on the Hammett σ is fulfilled for all the investigated substituents, including those that are conjugated with the reaction site [9]. On the basis of this the authors conclude that there is no influence of the resonance effect on the strength of the H-bond. However, it has been shown for secondary amines [10] that the involvement of the unshared pair of electrons of the nitrogen atom in conjugation with the π-elec-

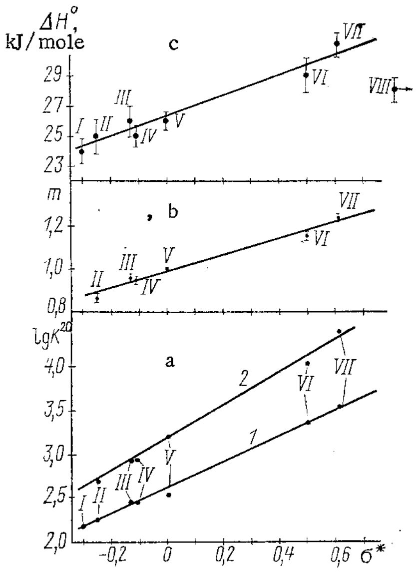

Fig. 4. Examples of the dependence of the thermodynamic parameters of H-complexes of NA on the Taft induction constants of the substituents σ^*. Dependences of log $K^{20°C}$ on σ^* (a), of the coefficients m (Table 4) on σ^* (b), and of ΔH° for complexes of NA with DMSO-D_6 on σ^* (c). For H-complexes of NA with DMSO-D_6 (1) and with HMPA (2).

TABLE 5. Parameters of the Correlation Equations log$\cdot K^{20°}_{RNHNO_2} = \rho\sigma^* + \log K_0$

Base	ρ	lg K_0	r	s
BA	0,97±0,09	0,67±0,03	0,988	0,06
AN-D_3	1,00±0,04	0,85±0,02	0,997	0,03
CH	1,17±0,02	1,20±0,01	0,999	0,02
DMAB	1,18±0,1	1,34±0,04	0,981	0,09
DMFA	1,46±0,1	2,01±0,04	0,988	0,09
DMAA	1,50±0,1	2,21±0,03	0,992	0,08
DMSO-D_6	1,49±0,04	2,61±0,01	0,998	0,04
HMPA	1,89±0,07	3,18±0,03	0,997	0,06

trons of the ring in the transition from aliphatic amines to aromatic amines leads to an increase in the proton donor capacity of the NH group. In the case of aliphatic N-nitroamines, the effect of conjugation has an opposite action; moreover, as can be seen from Fig. 4c, the decrease in the free energy of the complex is due chiefly to its enthalpy term. An analogous deviation of the values of pK_a of alkyl-N-nitroamines, measured in water, from linear correlation with σ^* in the direction of reduced acidity for substituents able to be conjugated with the reaction site was noted in [11], although in this case the effect is appreciably smaller. For measurements performed in aqueous medium, this anomaly was explained by a lowering of the energy of solvation of such anions, exceeding in absolute magnitude the gain in energy of delocalization of charge on account of conjugation with the substituent. In the case of a weakly solvating solvent CCl_4, such a large change in the enthalpy of complex formation cannot be explained by interaction of the complexes with the solvent. It can be assumed that both these phenomena have a common nature and are explained by the presence of a nitrogroup associated with the reaction site, which exerts a strong effect on the process of complex formation and proton transfer.

In conclusion, the authors would like to express gratitude to Yu. V. Serov for providing the preparations of a number of alkyl-N-nitroamines.

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ELECTRON-VIBRATIONAL INTERACTION IN POLYATOMIC MOLECULES. TAKING MOLECULAR SYMMETRY INTO ACCOUNT

V. I. Baranov

UDC 539.19

In the Herzberg–Teller approach [1] taking the electron-vibrational interaction into account within the framework of the adiabatic approximation reduces in its mathematical plan to the calculation of vibronic interaction integrals of the form

$$\langle u | A_\varkappa^t | u' \rangle , \qquad (1)$$

where $| u \rangle = \Psi_u(r)$; $| u' \rangle = \Psi_{u'}(r)$ are the electron wave functions of the states u and u' and the electron-vibrational interaction operator is equal to $A_\varkappa^t = \left(\frac{\partial U}{\partial Q_\varkappa^t}\right)_{Q_\varkappa^t=0}$; U(r, q) is the potential energy of the Coulomb attraction of electrons and nuclei; the derivative with respect to the normal vibrational coordinates of the t-th electronic state, $Q_\varkappa^t$, is taken at a point corresponding to the equilibrium geometry of the molecule. If the electron problem was solved in the MO basis of LCAO (with or without configuration interaction taken into account), then the integral (1) reduces to a corresponding linear combination of integrals over atomic orbitals (AO) μ and ν – $\langle \mu | A_\varkappa^t | \nu \rangle$ – and with the form of the function U and equivalence of the electrons taken into account we obtain [2]

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